THE HYDROTREATMENT OF COAL WITH $AlCl_3/HCl$ AND OTHER STRONG ACID MEDIA

J. Y. Low and D. S. Ross

Stanford Research Institute
333 Ravenswood Avenue, Menlo Park, California 94025

INTRODUCTION

Most current processes for upgrading coal to cleaner fuels require stringent reaction conditions of high temperatures and pressures. Less severe reaction conditions are needed to make coal upgrading economically feasible. The objective of this work was to investigate catalyst systems for upgrading of coal to clean fuels under moderated conditions. In this work, homogeneous acid catalysts are of particular interest because they allow intimate contact with the coal, they are not liable to coal ash fouling, and they are easily recovered from the coal ash.

The most common homogeneous catalysts studied in coal upgrading belong to the general class of molten salt catalysts, (1-5) and include halide salts of antimony, bismuth, aluminum, and many of the transition metals. Most often, these molten salts have been studied at high temperature, and in massive excess. (1-5) We have performed a systematic study of the use of some of these molten salts as the homogeneous acid catalysts for upgrading of coal at relatively low temperatures and moderate quantities.

In our initial work to establish relatively mild reaction conditions that would still give relatively good conversions, we conducted a series of experiments to determine the role of HCl, $AlCl_3$, and H_2 in coal hydrocracking. We examined the effects of temperature and residence time, studied catalyst/coal weight ratios of 1:1 to 3:1, and finally chose the standard reaction conditions for the screening of several acid catalysts. This paper summarizes the experimental studies and our results.

EXPERIMENTAL STUDIES

We used Illinois No. 6 coal, which was pulverized by ball milling under nitrogen to 60 mesh and then usually dried in a vacuum oven at 115°C overnight. Pennsylvania State University supplied beneficiated coal samples (PSOC-26) as well as an unbeneficiated sample (PSOC-25) for use in some experiments. The reactor used was either a rocking 500-ml autoclave fully lined with Teflon, or a 300-ml Hastelloy C Magne-Drive stirred autoclave from Autoclave Engineers. Standard tetrahydrofuran (THF) and pyridine solubilities were determined for the dried product coal by stirring a 0.50 g sample of the product coal in 50 ml THF or pyridine at room temperature for 1 hr, filtering the mixture in a medium porosity sintered glass filter, and then washing the residue with fresh solvent ($\sim$ 50 ml) until the washings were clear.

RESULTS AND DISCUSSION

In a series of runs in a rocking Teflon-lined autoclave, we first studied the role of HCl, $AlCl_3$, and H_2 in coal hydrocracking, using 5 g each of $AlCl_3$ and coal, at 190°C (just above the melting point of $AlCl_3$), for 15 and 5 hr. As shown in Figure 1, one or more of the three components were absent in Runs 1 to 6 and 9, and in each case no increase in THF and pyridine solubilities was observed. In Run 10, where all three components were present, solubilities increased substantially, suggesting that the $AlCl_3/HCl$ system was active. Runs 7 and 10 serve to assess the importance of HCl in the system under these conditions, however the results are not unequivocal. Here, the presence in the coal of proton sources, such as phenolic groups and traces of water, undoubtedly hydrolyzes some of the $AlCl_3$, producing HCl.

These runs indicate that no added HCl is required for coal hydrocracking at these lower temperatures.

At higher reaction temperatures (210°C) and shorter reaction time (5 hr) on the other hand, the added HCl clearly increases the conversion (Runs 21 and 25), suggesting that the effective catalyst in the system must contain the elements of HCl and $AlCl_3$.

Next, we studied the effect of potential H-donor hydrocarbons and temperature. We based our work on the results of Siskin,(5) who found that saturated, tertiary hydrocarbons serve as effective hydride donors in the strong acid-promoted hydrogenolysis of benzene. In our system they proved ineffective (Runs 17, 22, 24, and 26, Figure 1). Higher temperatures allowed shorter reaction times. The results for Run 18 (only 5 hr at 195°C) are comparable to those for Runs 7 and 10 (15 hr, 190°C). Runs at 195°C for 15 hr were significantly more effective, and the conversion for Run 12 at 5 hr and 210°C is about the same as that of Run 16 for 15 hr at 195°C.

Next, we studied the effects of the reaction period and catalyst to coal weight ratio on both the product character and the coal product yields in both the Teflon-lined and the Hastelloy C autoclaves. We first compared the effects of the catalyst/coal ratio and at a weight ratio of 1.0, the two systems yielded products with strikingly different pyridine solubilities: about 60% with the Teflon equipment. Increasing the catalyst/coal ratio to 2.0 increased solubilities to above 90%, but a further ratio increase actually caused solubilities to decrease slightly. The solid product recovery also decreased with increasing catalyst/coal ratio. At a 2.0 ratio, only about half the coal was recovered as a solid product. The other half was gasified. The softening point for the THF-soluble fraction was about 150°C; however, the pyridine-soluble fraction did not melt even up to 280°C. The coal products from the Teflon-lined reactor have consistently higher H/C ratio than those from the Hastelloy C reactor. We have no detailed explanation for the effect of autoclave surface on the results, but passivation of the metal surface by some minimum quantity of catalyst is part of the answer. Whatever the mechanism, the Teflon surface is helpful.

In runs over varying residence times in the Hastelloy C autoclave at a constant 2.0 catalyst/coal ratio, we observe significant differences in gasification. In runs of 5 hr down to 90 min, solid product recovery was 45 to 50%. In the 45 min runs, solid product recoveries were 66 to 72%. The H/C values for the isolated solid product coals for all six runs were remarkably similar, from 0.82 to 0.85. Similarly, all coal products have pyridine solubilities greater than 90%. The following scheme may explain these data.

The catalyst system gasifies some of the coal directly to methane and ethane. This result, and the effects of temperature on coal conversion, are shown in Table 1.

The Table shows data from runs at 210°C for reaction times from 45 min to 5 hr, and at 300°C for experiments all for 90 min.(the 210°C data are from an earlier phase of our work, where the gasification was not quantified. Thus the gasification was determined by difference. For the 300°C work, the quantities of gases and residue were determined independently, and thus the mass balances for these runs are not exactly 100%).

From the lower temperature results, it is seen that the degree of gasification increases with increasing reaction time. The solid coal products from these runs are all highly pyridine soluble, and have effectively the same H/C ratio, of 0.83 - 0.84. (The H/C ratio of the starting coal is 0.79).

The 300°C runs are all for 90 min, and experiments 83 and 85 show striking degrees of gasification. Fully 90+% of the carbon in the coal was converted to a

50:50 mixture of methane and ethane in these experiments. The next three runs were run without HCl present, and a cumulative effect of its absence is seen. The degrees of gasification decline severely, and the solid coal products recovered all have lessened pyridine solubilities and H/C ratios. A similar effect for HCl was observed by Kawa, et al.(2).

These data can be explained by the following scheme.

$$\underset{H/C = 0.79}{\text{Coal}} \xrightarrow[H_2/\text{Cat.}]{1} \underset{H/C = 0.83}{\text{Coal Prod.}} \xrightarrow[H_2/\text{Cat.}]{2} C_1 + C_2$$

$$\text{Coal} \xrightarrow[H_2/\text{no Cat.}]{3} \underbrace{\text{Char}}_{H/C = 0.75 \rightarrow 0.64}$$

Table 1

THE EFFECT OF RESIDENCE TIMES ON COAL GASIFICATION

(4 g Illinois No. 6 coal, 8 g $AlCl_3$, 500 psi HCl, 800 psi H_2, in a 300 ml stirred Hastelloy C autoclave)

	Run	Residence Time	Coal Residue % Rcvd	% Pyr Sol	H/C	% Coal Gasified
			210°C			
	67	5 hr	39	97	0.83	61[b]
	46[c]	"	48	87	0.82	52[b]
	41	4 hr	49	91	0.84	51[b]
	66	90 min	47	96	0.85	53[b]
	69[d]	45 min	72	93	0.82	28[b]
	71	"	66	97	0.84	34[b]
			300°C			
	83	90 min	18	78	0.72	96
	85	"	18	83	0.74	90
Run Without HCl	86	"	30	60	0.75	72
Run Without HCl	87	"	49	31	0.68	56
Run Without HCl	88	"	68	28	0.64	36

[a]Based on 4 g of coal.

[b]Assumed, based on unaccounted for material.

[c]Run with 3 g coal and 6 g $AlCl_3$.

Steps 1 and 2 are important in the presence of an effective catalyst and 3 becomes competitive with no effective catalyst present. At lower temperatures, $k_1 > k_2$. Thus, the hydrogen-rich, pyridine-soluble coal product accumulates and can be isolated. At high temperatures, the relative rates of Steps 1 and 2 are reversed, $k_2 > k_1$, and gasification is the major effect. Finally, when the elimination of HCl reduces the catalyst effectiveness, Steps 1 and 2 are suppressed and 3 becomes dominant. Thus

$AlCl_3$ alone is not only ineffective, it promotes char formation.* Moreover, with the lessening degrees of gasification, the coal residues appear to be increasingly cross-linked and depleted in hydrogen, possibly a result of chemistry at the autoclave surface.

Several acid catalysts were screened in two series of tests at two catalyst concentration levels, 210°C, 5 hr, 800 psi H_2, and 0.7 M HX (X = Br, Cl, or F). We found catalyst activity to vary considerably from one series to the next (Table 2). Catalyst coal ratio for the first series was 1:1. All catalysts studied at this ratio, except $AlBr_3$ and $AlCl_3$, were ineffective, reducing THF and pyridine solubilities significantly, perhaps because of internal condensation in the starting coal. The coal products in these runs are probably highly cross-linked. $AlCl_3$ was considerably more effective than $AlBr_3$, and HBr alone (Run 30) was, not surprisingly, ineffective. We found HCl to behave similarly (Run 4, Figure 1). Thus, these results indicate a catalyst effectiveness of $AlCl_3 > AlBr_3 \gg SbCl_3 \approx SbF_3 \approx ZnCl_2 \approx TaF_5 \approx NiSO_4 \approx CoSO_4 \approx HBr$.

Next we ran a more extensive series with the catalysts present at a constant ratio of 0.045 M catalyst/4 g coal, equivalent to 6 g $AlCl_3$/4 g coal. Here we found

$SbBr_3 \approx SbCl_3 > AlBr_3 > AlCl_3 > Ni(AA)_2 > TaF_5 \gg SbF_5 \approx MoCl_5 \approx WCl_6$

(AA = acetylacetonate). In this second series we found first that TaF_5, which Siskin (6) found to effectively hydrocrack benzene to mixed hexanes, is not at all effective under our conditions. Similarly, $ZnCl_2$, the well known coal conversion catalyst, is not effective under these conditions, perhaps because under our relatively mild conditions, $ZnCl_2$ is not molten (mp, 283°C). Finally, the favorable antimony bromide and chloride results are similar to those reported by Shell (1).

In Run 35 (Table 2), with $AlCl_3$/HCl, we used unbeneficiated coal. Here, the THF solubility of the product coal increased by almost a factor of 2, to 40%. The pyridine solubility increased slightly, to 66%. Since pyridine is generally a better solvent for coal liquids than is THF, the considerable increase in THF solubility suggests that more lower molecular weight products are obtained when unbeneficiated coal is used. Also, the mineral matter present in the unbeneficiated coal clearly aids in the acid-catalyzed hydrocracking process, suggesting that the mineral matter in the coal is an effective catalyst under acid conditions.

SUMMARY OF RESULTS

We now have established a set of relatively mild experimental conditions for coal conversion and have identified several homogeneous acid catalysts, which under these conditions can convert the coal almost completely to pyridine-soluble material. The reaction conditions for $AlCl_3$ are 210°C, 45 min, 2:1 $AlCl_3$/coal weight ratio, 500 psi H_2, 800 psi HCl. Also, we have observed that with 1:1 catalyst/coal weight ratio, the effectiveness of the catalysts for conversion is

$AlCl_3 > AlBr_3 \gg SbCl_3 \approx SbF_3 \approx ZnCl_2 \approx TaF_5 \approx NiSO_4 \approx CoSO_4$.

When a constant molar ratio of catalyst is used, the order is:

$SbBr_3 \approx SbCl_3 > AlBr_3 > AlCl_3 > Ni(AA)_2 > TaF_5 \gg SbF_5 \approx MoCl_5 \approx WCl_6$.

We have discovered that adding HCl to $AlCl_3$ significantly enhances conversion for runs with short residence time (5 hr or shorter) at 210°C. Under similar reaction conditions, a Teflon-lines reactor yields coal products with greater H/C values than does the Hastelloy C reactor. Residence time also has a significant effect on gasification. More than 50% of the coal is gasified for residence times of 95 min or longer; 30% is gasified at 45 min. Finally, we have established that at 300°C reaction temperature, $AlCl_3$/coal weight ratio of 2:1, and with HCl added, about 90% of the coal is converted to methane and ethane.

*The cumulative effect of HCl absence is explained by the need for passivated reactor surfaces. When these reactions are run in fully Teflon-lined reactors, the results are significantly improved. Considerably lower catalyst/coal ratios provide results comparable to those shown here.

Table 2

TREATMENT OF ILLINOIS NO. 6 COAL WITH H_2/STRONG ACID SYSTEMS

Run #	Catalyst System	Pressure (psi)		Solubilities (%)[b]	
		H_2	HX	THF	Pyr
(a) Constant Weight[a]					
28	$AlCl_3/HCl/H_2$	800	500	23	58
35	$AlCl_3/HCl/H_2$[c]	800	500	40	66
29	$AlBr_3/HBr/H_2$	980	33g	9	27
27	$AlBr_3/HBr/H_2$	820	50g	11	32
30	HBr/H_2	1000	31g	2	6
31	$SbCl_3/HCl/H_2$	800	500	-	1
32	$TaF_5/HF/H_2$	1100	22g	-	13
33	$SbF_3/HF/H_2$	1100	16g	< 1	4
44	$ZnCl_2/HCl/H_2$	800	500	-	9
56	$CoSO_4/H_2SO_4$	1300	68.6g	< 1	< 1
57	$NiSO_4/H_2SO_4$	1300	68.6g	< 1	< 1
(b) Constant Molar Quantity[d]					
45	$AlCl_3/HCl/H_2$	800	500	25	47
48	$AlBr_3/HBr/H_2$	1100	70g	30	59
49	$SbCl_3/HCl/H_2$	800	500	-	∿100
50	$TaF_5/HF/H_2$	900	14g	11	20
52	$SbF_5/HF/H_2$	1150	14g	< 1	< 1
54	$MoCl_5$	1300	-	8	16
55	WCl_6	1300	-	6	12
61	$SbBr_3/HBr$	850	59g	43	∿100
62	$Ni(AA)_2/HCl$	800	500	ND[e]	38
70	$MoCl_5/HCl$	800	500	< 1	4

[a]In this series of experiments, 5 g of coal was treated at 210°C for 5 hr in a rocking Teflon-lines autoclave. [b] Moisture-ash-free basis. [c] Unbeneficiated coal was used. [d] These experiments used 0.045 moles of catalyst per 4 g coal. A stirred Hastelloy C autocalve was used. [e] NO = Not determined.

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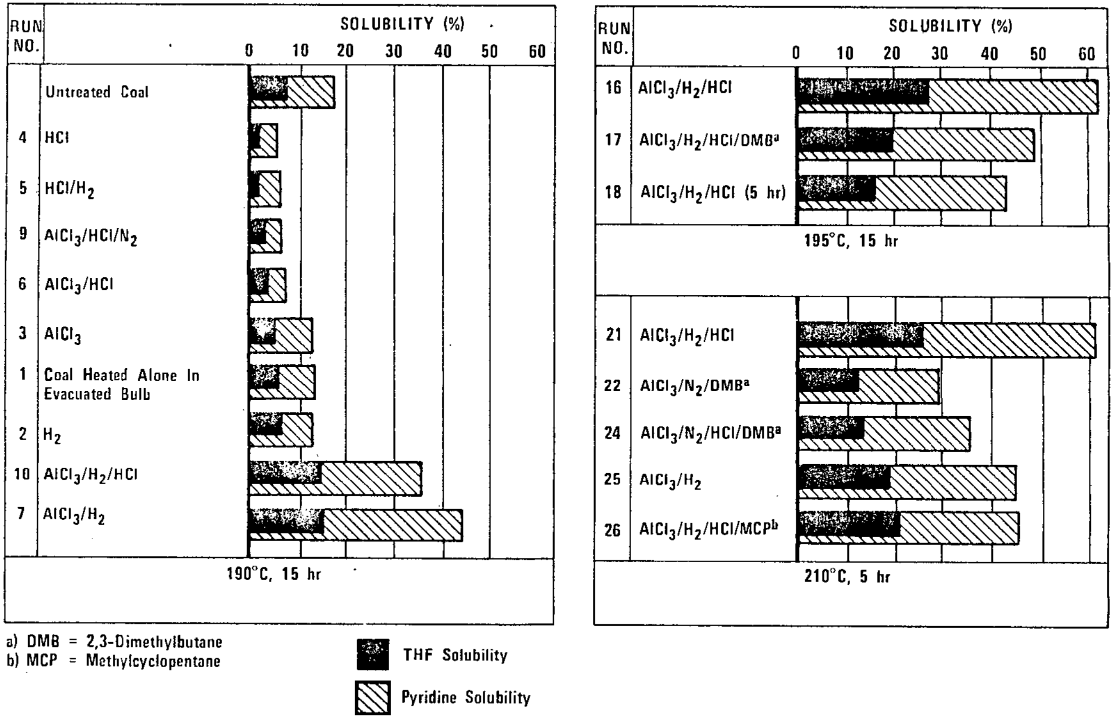

a) DMB = 2,3-Dimethylbutane
b) MCP = Methylcyclopentane

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FIGURE 1 ACID-CATALYZED HYDROCRACKING OF BENEFICIATED ILLINOIS NO. 9 COAL